

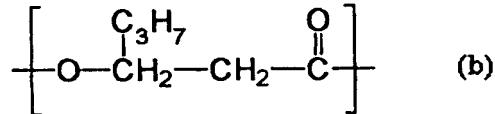
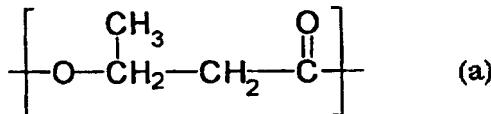
PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ :	A1	(11) International Publication Number: WO 95/20621 (43) International Publication Date: 3 August 1995 (03.08.95)
C08J 5/18, A61L 15/26, 15/62, C08G 63/08		
(21) International Application Number:	PCT/US95/00585	(81) Designated States: AM, AU, BB, BG, BR, BY, CA, CN, CZ, EE, FI, GE, HU, JP, KG, KP, KR, KZ, LK, LR, LT, LV, MD, MG, MN, MX, NO, NZ, PL, RO, RU, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ).
(22) International Filing Date:	13 January 1995 (13.01.95)	
(30) Priority Data:	08/188,271 28 January 1994 (28.01.94) US	
(71) Applicant:	THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).	Published <i>With international search report.</i>
(72) Inventor:	NODA, Isao; 1568 Hunter Road, Fairfield, OH 45014 (US).	
(74) Agents:	REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).	

(54) Title: BIODEGRADABLE 3-POLYHYDROXYBUTYRATE/3-POLYHYDROXYHEXANOATE COPOLYMER FILMS



(57) Abstract

The present invention relates to a film comprising a biodegradable copolymer, wherein the copolymer comprises at least two randomly repeating monomer units (RRMU) wherein the first RRMU monomer unit has structure (a) and the second RRMU has structure (b) wherein at least 50 % of the RRMUs have the structure of the first RRMU. The present invention further relates to an absorbent article comprising a liquid pervious topsheet, a biodegradable liquid impervious backsheets comprising the above film, and an absorbent core positioned between the topsheet and the backsheets.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

Biodegradable 3-polyhydroxybutyrate/3-polyhydroxyhexanoate copolymer films

TECHNICAL FIELD

The present invention relates to biodegradable copolymers; films comprising the copolymers; and disposable absorbent articles such as diapers, sanitary napkins and pantiliners, comprising such films.

BACKGROUND

A wide variety of absorbent articles designed to be efficient for the absorption of body fluids such as blood, urine, menses, and the like, are known. Disposable products of this type generally comprise some sort of fluid-permeable topsheet material, an absorbent core, and a fluid-impermeable backsheet material. Heretofore, such absorbent structures have been prepared using, for example, topsheet materials prepared from woven, non-woven, or porous formed-film polyethylene or polypropylene materials. Backsheet materials typically comprise flexible polyethylene sheets. Absorbent core materials typically comprise wood pulp fibers or wood pulp fibers in combination with absorbent gelling materials. One aspect of such absorbent articles that has recently been considered is their disposability. Although such products largely comprise materials which would be expected ultimately to degrade, and although products of this type contribute only a very small percentage of the total solid waste materials generated by consumers each year, nevertheless, there is currently a perceived need to devise such disposable products from materials which are compostable.

A conventional disposable absorbent product is already to a large extent compostable. A typical disposable diaper, for example, consists of about 80% of compostable materials, e.g., wood pulp fibers, and the like. In the composting process soiled disposable absorbent articles are shredded and commingled with organic waste prior to the composting per se. After composting is complete, the non-compostable particles are screened out. In this manner even today's absorbent articles can successfully be processed in commercial composting plants.

Nevertheless, there is a need for reducing the amount of non-compostable materials in disposable absorbent articles. There is a particular need to replace polyethylene backsheets in absorbent articles

with liquid impervious films of compostable material, because the backsheet is typically one of the largest non-compostable components of a conventional disposable absorbent article.

In addition to being compostable, the films employed as backsheets for absorbent articles must satisfy many other performance requirements. For example, the resins should be thermoplastic such that conventional film processing methods can be employed. These methods include cast film and blown film extrusion of single layer structures and cast or blown film coextrusion of multilayer structures. Other methods include extrusion coating of one material on one or both sides of a compostable substrate such as another film, a non-woven fabric, or a paper web.

Still other properties are essential in product converting operations where the films are used to fabricate absorbent articles. Properties such as tensile strength, tensile modulus, tear strength, and thermal softening point determine to a large extent how well a film will run on converting lines.

In addition to the aforementioned properties, still other properties are needed to meet the end user requirements of the absorbent article. Film properties such as impact strength, puncture strength, and moisture transmission are important since they influence the absorbent article's durability and containment while being worn.

Once the absorbent article is disposed of and enters a composting process, other properties become important. Regardless of whether incoming waste is preshredded or not, it is important that the film or large film fragments undergo an initial breakup to much smaller particles during the initial stages of composting. Otherwise, the films or large fragments may be screened out of the compost stream and may never become part of the final compost.

In the past, the biodegradability and physical properties of a variety of polyhydroxyalkanoates have been studied. Polyhydroxyalkanoates are polyester compounds produced by a variety of microorganisms, such as bacteria and algae. While polyhydroxyalkanoates have been of general interest because of their biodegradable nature, their actual use as a plastic material has been hampered by their thermal instability. For example, poly-3-hydroxybutyrate (PHB) is a natural energy-storage product of bacteria and algae, and is present in discrete granules within the cell cytoplasm. However, unlike other biologically synthesized polymers such as proteins and polysaccharides, PHB is thermoplastic having a high degree of

crystallinity and a well-defined melt temperature of about 180°C. Unfortunately, PHB becomes unstable and degrades at elevated temperatures near its melt temperature. Due to this thermal instability, commercial applications of PHB have been extremely limited.

As a result, investigators have studied other polyhydroxyalkanoates such as poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), in the hopes of discovering a polyhydroxyalkanoate having sufficient thermal stability and other suitable chemical and physical properties for use in practical applications. Unfortunately, polyhydroxyalkanoates such as PHB and PHBV are difficult to process into films suitable for backsheet applications. As previously discussed, the thermal instability of PHB makes such processing nearly impossible. Furthermore, the slow crystallization rates and flow properties of PHB and PHBV make film processing difficult. Examples of PHB homopolymer and PHBV copolymers are described in U.S. Patent 4,393,167, Holmes et al., issued July 12, 1983, and U.S. Patent 4,880,592, issued November 14, 1989. Copolymers of PHBV are commercially available from Imperial Chemical Industries under the tradename BIOPOL. PHBV copolymers are currently produced with valerate contents ranging from about 5 to about 24 mol%. Increasing valerate content decreases the melt temperature, crystallinity, and stiffness of the polymer. An overview of BIOPOL technology is provided in BUSINESS 2000+ (Winter, 1990).

Due to the slow crystallization rate, a film made from PHBV will stick to itself even after cooling; a substantial fraction of the PHBV remains amorphous and tacky for long periods of time. In cast film operations, where the film is immediately cooled on chill rolls after leaving the film die, molten PHBV often sticks to the rolls restricting the speed at which the film can be processed, or even preventing the film from being collected. In blown films, residual tack of the PHBV causes the tubular film to stick to itself after it has been cooled and collapsed for winding.

U.S. Patent 4,880,592, Martini et al., issued November 14, 1989, discloses a means of achieving a PHBV monolayer film for diaper backsheet applications by coextruding the PHBV between two layers of sacrificial polymer, for example a polyolefin, stretching and orienting the multilayer film, and then stripping away the polyolefin layers after the PHBV has had time to crystallize. The remaining PHBV film is then laminated to either water soluble films or water insoluble films such as polyvinylidene

chloride or other polyolefins. Unfortunately, such drastic and cumbersome processing measures are necessary in an attempt to avoid the inherent difficulties associated with processing PHBV into films.

Based on the foregoing, there is a need for disposable absorbent articles (e.g., diapers) with increased biodegradability. To satisfy this need, there is a preliminary need for a biodegradable copolymer which is capable of being easily processed into a film for use in such disposable sanitary garments.

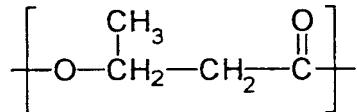
Objects of the Invention

It is an object of the present invention to provide a film comprising a biodegradable polyhydroxyalkanoate.

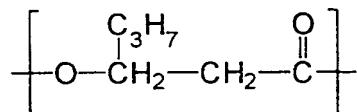
It is also an object of the present invention to provide a disposable sanitary garment comprising a film comprising a biodegradable PHA.

SUMMARY

The present invention relates to a film comprising a biodegradable copolymer, wherein the copolymer comprises at least two randomly repeating monomer units (RRMU) wherein the first RRMU has the structure



and the second RRMU has the structure



wherein at least 50% of the RRMUs have the structure of the first RRMU.

The present invention further relates to an absorbent article comprising a liquid pervious topsheet, a biodegradable liquid impervious backsheet comprising the above film, and an absorbent core positioned between the topsheet and the backsheet.

DETAILED DESCRIPTION

The present invention answers the need for a biodegradable copolymer which is capable of being easily processed into a film. The present invention further answers the need for disposable absorbent articles with increased biodegradability.

As used herein, "ASTM" means American Society for Testing and Materials.

As used herein, "comprising" means that other steps and other ingredients which do not affect the end result can be added. This term encompasses the terms "consisting of" and "consisting essentially of".

As used herein, "alkyl" means a saturated carbon-containing chain which may be straight or branched; and substituted (mono- or poly-) or unsubstituted.

As used herein, "alkenyl" means a carbon-containing chain which may be monounsaturated (i.e., one double bond in the chain) or polyunsaturated (i.e., two or more double bonds in the chain); straight or branched; and substituted (mono- or poly-) or unsubstituted.

As used herein, "PHA" means a polyhydroxyalkanoate of the present invention.

As used herein, "PHB" means the homopolymer poly-3-hydroxybutyrate.

As used herein, "PHBV" means the copolymer poly(3-hydroxybutyrate-co-3-hydroxyvalerate).

As used herein, "biodegradable" means the ability of a compound to ultimately be degraded completely into CO₂ and water or biomass by microorganisms and/or natural environmental factors.

As used herein, "compostable" means a material that meets the following three requirements: (1) the material is capable of being processed in a composting facility for solid waste; (2) if so processed, the material will end up in the final compost; and (3) if the compost is used in the soil, the material will ultimately biodegrade in the soil.

For example, a polymer film material present in solid waste submitted to a composting facility for processing does not necessarily end up in the final compost. Certain composting facilities subject the solid waste stream to air classification prior to further processing, in order to separate paper and other materials. A polymer film would most probably be separated from the solid waste stream in such an air classification and therefore not be processed in the composting facility. Nevertheless, it may still be a "compostable" material according to the above definition because it is "capable" of being processed in a composting facility.

The requirement that the material ends up in the final compost typically means that it undergoes a form of degradation in the composting process. Typically, the solid waste stream will be subjected to a shredding step in an early phase of the composting process. As a result, the polymer

film will be present as shreds rather than a sheet. In the final phase of the composting process, the finished compost will be subjected to a screening step. Typically, the polymer shreds will not pass through the screens if they have retained the size they had immediately after the shredding step. The compostable materials of the present invention will have lost enough of their integrity during the composting process to allow partially degraded shreds to pass through the screens. However, it is conceivable that a composting facility might subject the solid waste stream to a very rigorous shredding and a rather coarse screening, in which case nondegradable polymers like polyethylene would meet requirement (2). Therefore, meeting requirement (2) is not enough for a material to be compostable within the present definition.

What distinguishes the compostable material as defined herein from material like polyethylene is requirement (3), that the material ultimately biodegrade in the soil. This biodegradability requirement is not essential to the composting process or the use of composting soil. Solid waste and the compost resulting therefrom may contain all kinds of nonbiodegradable materials, for example, sand. However, to avoid a build up of man-made materials in the soil, it is required herein that such materials be fully biodegradable. By the same token, it is not at all necessary that this biodegradation be fast. As long as the material itself and intermediate decomposition products are not toxic or otherwise harmful to the soil or crops, it is fully acceptable that their biodegradation takes several months or even years, since this requirement is present only to avoid an accumulation of man-made materials in the soil.

All copolymer composition ratios recited herein refer to mole ratios, unless specifically indicated otherwise.

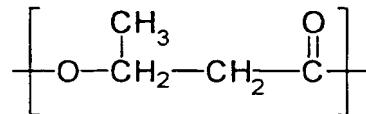
Films

The present invention relates to biodegradable copolymers which are surprisingly easy to process into films as compared to the homopolymer PHB and copolymer PHBV. Prior to Applicants' invention, polyhydroxyalkanoates studied for use in commercial plastics production presented significant impediments to their use in plastics. As discussed above, polyhydroxyalkanoates such as PHB and the copolymer PHBV are difficult to process due to their thermal instability. Furthermore, such polyhydroxyalkanoates were especially difficult to process into films due to their slow crystallization rate. Applicants have found that PHA copolymers

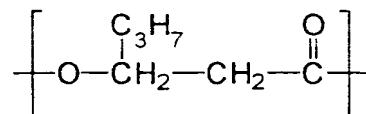
of the present invention, which comprise a second RRMU as defined above having an alkyl branch of at least three (3) carbons, are surprisingly easier to process into films, especially as compared to PHB or PHBV. Applicants surprisingly discovered, such linear, random copolymers with a limited number of medium sized (e.g., C₃-C₁₉) branches provide, in addition to biodegradability, the following properties, particularly as compared to PHB or PHBV: a) a lower melt temperature, b) a lower degree of crystallinity, and c) an improved melt rheology.

Without being bound by theory, Applicants believe characteristics a) and b) are achieved by exclusion of the second RRMU from the crystal lattice of the first RRMU, thereby resulting in a decreased temperature for thermal processing and improved stiffness and elongation properties. Again, without being bound by theory, Applicants believe characteristic c) is achieved by increased entanglement between the copolymer chains due to the side chains of the second RRMU. Such increased entanglement may occur by increased hydrodynamic volume of the copolymer (e.g., the second monomer unit creates kinks in the helical structure), the "hooking" or "catching" of the side chains on different copolymer backbones while in the melt, or the decreased chain scission due to the lower T_m (i.e., the enlarged thermal process window).

Biodegradable PHAs useful for processing into the films of the present invention comprises at least two randomly repeating monomer units (RRMU) wherein the first RRMU has the structure

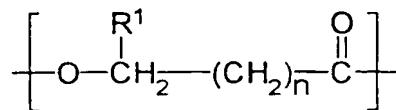


and the second RRMU has the structure



wherein at least 50% of the RRMUs have the structure of the first RRMU.

In a preferred embodiment, the PHA comprises one or more additional RRMUs having the structure



wherein R¹ is H, or a C₂ or C₄, C₅, C₆, C₇, C₈, C₉, C₁₀, C₁₁, C₁₂, C₁₃, C₁₄, C₁₅, C₁₆, C₁₇, C₁₈, or C₁₉ alkyl or alkenyl; and n is 1 or 2.

As used herein, "film" means an extremely thin continuous piece of a substance having a high length to thickness ratio and a high width to thickness ratio. While there is no requirement for a precise upper limit of thickness, a preferred upper limit would be about 0.254 mm, more preferably still 0.01 mm, more preferably still 0.005 mm. The protective value of any film depends on its being continuous, i.e., without holes or cracks, since it must be an efficient barrier to molecules such as atmospheric water vapor and oxygen. In a preferred embodiment of the present invention, the film of the present invention is liquid impervious and suitable for use in absorbent disposable sanitary garments such as disposable diapers, feminine hygiene products and the like. More preferably, films of the present invention, in addition to increased biodegradability and/or compostability, have the following properties:

- a) a machine direction (MD) tensile modulus from about 10,000 to about 100,000 lbs./sq. in. (6.895×10^8 dynes/sq. cm to 6.895×10^9 dynes/sq. cm),
- b) a MD tear strength of at least 70 grams per 25.4 μm of thickness,
- c) a cross machine direction (CD) tear strength of at least 70 grams per 25.4 μm of thickness,
- d) an impact strength of at least 12 cm as measured by falling ball drop,
- e) a moisture transport rate less than about 0.0012 grams per square centimeter per 16 hours,
- f) a modulus at 60°C of at least 5.52×10^7 dynes/sq. cm (800 lbs./sq. in), and
- g) a thickness from about 12 μm to about 75 μm .

Methods for testing for such performance criteria are discussed in more detail below.

Performance Criteria and Test Methods for Films

For a film to perform satisfactorily as a compostable disposable diaper backsheet, it must be made of resins or structures that are biodegradable and it must demonstrate the following properties of high strength, adequate fluid barrier, appropriate modulus or flexibility, and adequately high melting point.

The backsheets of disposable diapers must have sufficient strength both to process on a high speed disposable diaper converting machine and to provide a "wetproof" barrier in use on an infant. It must be sufficiently wetproof so that the clothing or bedding, either that of the infant or of the caregiver, is not wet or soiled. It must have a modulus or flexibility that is, at the same time, low enough to be a soft, pleasing material to be used as the outer covering of an infant diaper yet high enough to handle easily on high speed disposable diaper converters without wrinkling, folding, or creasing. It must have sufficient resistance to heat such that it will not deform, melt, or permanently lose strength in typical hot storage conditions or lose its integrity on high speed disposable diaper converters which typically use hot melt adhesives to bond the components of a disposable diaper together.

Films that are sufficiently strong to be suitable as biodegradable and/or compostable backsheets for disposable diapers preferably demonstrate two properties: (a) resistance to rupture from a dropped weight and (b) resistance to tearing in both the machine direction of manufacture and the cross-machine direction of manufacture. Preferred backsheets of the present invention can withstand the drop of a spherical steel ball of about 19 millimeters in diameter and 27.6 to 28.6 gram mass from a height of 12 centimeters so that at least 50% of the tests result in no rupture of any size (deformation is acceptable). Preferred materials are those that exhibit 50% or less failures from a height of more than 20 centimeters. Similarly, acceptable backsheets of the present invention demonstrate an average tear propagation resistance of 70 grams per 25.4 micron thickness of material in both the machine direction and cross-machine direction of manufacture when a standard Elmendorf pendulum-type test device, such as Elmendorf Model No. 60-100, is employed against 16 plies of material which have been prepared with a cut or notch according to TAPPI Method T 414om-88. More preferable are those backsheets that demonstrate tear propagation resistances of 200 or more grams per 25.4 micron thickness in the cross-machine direction because these are particularly good at avoiding a tendency to fail in use by splitting.

It has also been found that films of sufficient barrier to moisture transport are those that permit less than 0.0012 grams of synthetic urine to pass into an absorbent paper towel per square centimeter of area per 25.4 micron thickness for every 16 hours of time when the test film is located between the absorbent paper towel and a typical absorbent gelling material-

containing diaper core and a pressure simulating that of a baby. The specific conditions of the test are that the area of the core is larger than that of the test material, the core is loaded with synthetic urine to its theoretical capacity and it is under a weight of about 35 g/cm^2 (0.5 psi).

It has also been found that materials of sufficient heat resistance demonstrate a Vicat softening point of at least 45°C . Vicat softening is tested using a Heat Distortion Apparatus Model No. CS-107 or equivalent and a modification of ASTM D-1525. The modification is in the preparation of the sample. A 19 square millimeter size film of 4.5 to 6.5 mm thickness is prepared for Vicat needle penetration tests by melting the material to be tested into a mold using a temperature of 120°C and pressure of $7.031 \times 10^5 \text{ g/cm}^2$ (10,000 psi) (using a Carver or similar press) for two minutes after a warm-up period of at least 2 minutes. The Vicat softening point is the temperature at which a flat-ended needle of 1 sq. mm circular cross section will penetrate the sample to a depth of 0.1 cm under a load 1000 g using a uniform temperature rise rate of 50°C per hour.

It has also been found that materials of sufficient machine direction modulus demonstrate a 1% secant-type modulus above at least about $6.895 \times 10^8 \text{ dynes/cm}^2$ (10,000 psi) and below about $6.895 \times 10^9 \text{ dynes/cm}^2$ (100,000 psi). The test is performed on an electronic tensile test machine such as the Instron Model 4201. A 2.54 cm wide strip of material, preferably of 0.00254 cm in thickness, is cut to a length of about 30 cm with the longer dimension parallel to the machine direction of the material. The test strip is clamped into the jaws of the tensile testor so that the gauge or actual length of the material tested is 25.4 cm. The jaws are separated at a slow speed in the range of 2.54 cm per minute to 25.4 cm per minute and a stress-strain curve is plotted on a chart within an attached recording device. The 1% secant modulus is determined by reading the stress or tensile from the chart at the 1% elongation strain point. For example, the 1% strain point is achieved when the distance between jaws has increased by 0.254 cm. When the jaws are separating at the rate of 2.54 cm per minute and the recording device is running at a speed of 25.4 cm per minute, the 1% strain point will be located at a distance of 2.54 cm from the initial point. The tensile response is divided by the thickness of the sample material if it is not 0.00254 cm in thickness. Particularly soft, and therefore preferred, materials exhibit 1% secant moduli in the range of 6.895×10^8 to $2.068 \times 10^9 \text{ dynes/cm}^2$ (10,000 to 30,000 psi).

Since absorbent articles may experience temperatures as high as 140°F (60°C) during warehouse storage or shipping in trucks or railcars, it is important that the backsheet film and other components retain their integrity at these temperatures. Although it is expected that the modulus of the films will decrease somewhat between 20°C and 60°C, the modulus should not decrease too far and allow the film to deform in the package before it reaches the end user.

For example, a polyethylene backsheet with a room temperature modulus of about 4×10^9 dynes/cm² (58,000 psi) may have a 60°C modulus of 1.2×10^9 dynes/cm² (18,560 psi) which is acceptable. A softer polyethylene backsheet with a room temperature modulus of about 8.0×10^8 dynes/cm² (11,600 psi) may have a 60°C modulus of about 3.5×10^8 dynes/cm² (5,076 psi) which is still acceptable. In general, an acceptable backsheet film of the present invention will have a 60°C modulus of at least 5.52×10^7 dynes/cm² (800 psi).

The modulus dependence on temperature, also called a modulus/temperature spectrum, is best measured on a dynamic mechanical analyzer (DMA) such as a Perkin Elmer 7 Series/Unix TMA 7 Thermomechanical Analyzer equipped with a 7 Series/Unix DMA 7 Temperature/Time software package, hereinafter referred to as the DMA 7, available from the Perkin-Elmer Corporation of Norwalk, Connecticut. Many other types of DMA devices exist, and the use of dynamic mechanical analysis to study the modulus/temperature spectra of polymers is well known to those skilled in the art of polymer (or copolymer) characterization. This information is well summarized in two books, the first being DYNAMIC MECHANICAL ANALYSIS OF POLYMERIC MATERIAL, MATERIALS SCIENCE MONOGRAPHS VOLUME 1 by T. Murayama (Elsevier Publishing Co., 1978) and the second being MECHANICAL PROPERTIES OF POLYMERS AND COMPOSITES, VOLUME 1 by L.E. Nielsen (Marcel Dekker, 1974).

The mechanism of operation and procedures for using the DMA 7 are found in Perkin-Elmer Users' Manuals 0993-8677 and 0993-8679, both dated May, 1991. To those skilled in the use of the DMA 7, the following run conditions should be sufficient to replicate the 60°C modulus data presented hereinafter.

To measure the modulus/temperature spectrum of a film specimen, the DMA 7 is set to run in temperature scan mode and equipped with an extension measuring system (EMS). A film specimen approximately 3 mm

wide, 0.0254 mm thick, and of sufficient length to allow 6 to 8 mm of length between the specimen grips is mounted in the EMS. The apparatus is then enclosed in an environmental chamber swept continuously with helium gas. Stress is applied to the film in the length direction to achieve a deformation or strain of 0.1 percent of the original length. A dynamic sinusoidal strain is applied to the specimen at a frequency of 5 cycles per second. In the temperature scan mode, the temperature is increased at a rate of 3.0°C/minute from 25°C to the point where the specimen melts or breaks, while the frequency and stress are held constant. Temperature-dependent behavior is characterized by monitoring changes in strain and the phase difference in time between stress and strain. Storage modulus values in Pascals are calculated by the computer along with other data and displayed as functions of temperature on a video display terminal. Normally the data are saved on computer disk and a hard copy of the storage modulus/temperature spectrum printed for further review. The 60°C modulus is determined directly from the spectrum.

Method of Film Manufacture

The films of the present invention used as backsheets having increased biodegradability and/or compostability may be processed using conventional procedures for producing single or multilayer films on conventional film-making equipment. Pellets of the PHAs of the present invention can be first dry blended and then melt mixed in a film extruder. Alternatively, if insufficient mixing occurs in the film extruder, the pellets can be first dry blended and then melt mixed in a precompounding extruder followed by repelletization prior to film extrusion.

The PHAs of the present invention can be melt processed into films using either cast or blown film extrusion methods both of which are described in PLASTICS EXTRUSION TECHNOLOGY--2nd Ed., by Allan A. Griff (Van Nostrand Reinhold--1976). Cast film is extruded through a linear slot die. Generally the flat web is cooled on a large moving polished metal roll. It quickly cools, and peels off this first roll, passes over one or more auxiliary cooling rolls, then through a set of rubber-coated pull or "haul-off" rolls, and finally to a winder. A method of making a cast backsheet film for the absorbent articles of the present invention is described in an example below.

In blown film extrusion, the melt is extruded upward through a thin annular die opening. This process is also referred to as tubular film

extrusion. Air is introduced through the center of the die to inflate the tube and thereby causing it to expand. A moving bubble is thus formed which is held at a constant size by control of internal air pressure. The tube of film is cooled by air, blown through one or more chill rings surrounding the tube. The tube is then collapsed by drawing it into a flattening frame through a pair of pull rolls and into a winder. For backsheet applications the flattened tubular film is subsequently slit open, unfolded, and further slit into widths appropriate for use in products.

Both cast film and blown film processes can be used to produce either monolayer or multilayer film structures. For the production of monolayer films from a single thermoplastic material or blend of thermoplastic components only a single extruder and single manifold die are required.

For the production of multilayer films of the present invention, coextrusion processes are preferably employed. Such processes require more than one extruder and either a coextrusion feedblock or multi-manifold die system or combination of the two to achieve the multilayer film structure.

U.S. Patents 4,152,387, and 4,197,069, disclose the feedblock principle of coextrusion. Multiple extruders are connected to the feedblock which employs moveable flow dividers to proportionally change the geometry of each individual flow channel in direct relation to the volume of polymer passing through said flow channels. The flow channels are designed such that at their point of confluence, the materials flow together at the same flow rate and pressure eliminating interfacial stress and flow instabilities. Once the materials are joined in the feedblock, they flow into a single manifold die as a composite structure. It is important in such processes that the melt viscosities and melt temperatures of the materials do not differ too greatly; otherwise flow instabilities can result in the die leading to poor control of layer thickness distribution in the multilayer film.

An alternative to feedblock coextrusion is a multi-manifold or vane die as disclosed in aforementioned U.S. Patents 4,152,387, 4,197,069, and in U.S. Patent 4,533,308. Whereas in the feedblock system melt streams are brought together outside and prior to entering the die body, in a multi-manifold or vane die each melt stream has its own manifold in the die where the polymers spread independently in their respective manifolds. The melt streams are married near the die exit with each melt stream at full die width. Moveable vanes provide adjustability of the exit of each flow channel in

direct proportion to the volume of material flowing through it, allowing the melts to flow together at the same linear flow rate, pressure, and desired width.

Since the melt flow properties and melt temperatures of the processed materials may vary widely, use of a vane die has several advantages. The die lends itself toward thermal isolation characteristics wherein materials of greatly differing melt temperatures, for example up to 175°F (80°C), can be processed together.

Each manifold in a vane die can be designed and tailored to a specific polymer (or copolymer). Thus the flow of each polymer is influenced only by the design of its manifold, and not by forces imposed by other polymers. This allows materials with greatly differing melt viscosities to be coextruded into multilayer films. In addition, the vane die also provides the ability to tailor the width of individual manifolds, such that an internal layer, for example a water soluble biodegradable polymer like Vinex 2034, can be completely surrounded by water insoluble materials leaving no exposed edges susceptible to water. The aforementioned patents also disclose the combined use of feedblock systems and vane dies to achieve more complex multilayer structures.

The multilayer films of the present invention may comprise two or more layers. In general, balanced or symmetrical three-layer and five-layer films are preferred. Balanced three-layer multilayer films comprise a center core layer and two identical outer layers, wherein said center core layer is positioned between said two outer layers. Balanced five-layer multilayer films comprise a center core layer, two identical tie layers, and two identical outer layers, wherein said center core layer is positioned between said two tie layers, and a tie layer is positioned between said center core layer and each outer layer. Balanced films, though not essential to the films of the present invention, are less prone to curling or warping than unbalanced multilayer films.

In three layer films, the center core layer may comprise 30 to 80 percent of the films' total thickness and each outer layer comprises 10 to 35 percent of the films' total thickness. Tie layers, when employed, each comprise from about 5 percent to about 10 percent of the films' total thickness.

Crystallinity

The volume percent crystallinity (Φ_C) of a semi-crystalline polymer (or copolymer) often determines what type of end-use properties the polymer possesses. For example, highly (greater than 50%) crystalline polyethylene polymers are strong and stiff, and suitable for products such as plastic milk containers. Low crystalline polyethylene, on the other hand, is flexible and tough, and is suitable for products such as food wraps and garbage bags. Crystallinity can be determined in a number of ways, including x-ray diffraction, differential scanning calorimetry (DSC), density measurements, and infrared absorption. The most suitable method depends upon the material being tested.

X-ray diffraction is most appropriate when little is known about the thermal properties of the material and crystal structural changes may occur. The basic principle relies on the fact that amorphous parts of the material scatter x-rays in a diffuse or broad range of angles while crystals diffract x-rays into sharp, precisely defined angles. The total scattered intensity is constant, however. This allows calculation of the amount of crystalline material in a sample if the amorphous and crystalline diffracted intensities can be separated. A very precise method has been developed by Ruland, which can detect differences in percent crystallinity as small as 2% (see Vonk, C., F.J. Balta-Calleja, X-RAY SCATTERING FROM SYNTHETIC POLYMERS, Elsevier: Amsterdam, (1989); and Alexander, L., X-RAY DIFFRACTION METHODS IN POLYMER SCIENCE, Robert Kreiger Pub. Co., New York, (1979)).

Upon melting, crystals require a fixed amount of heat at the melting temperature transforming from crystalline to molten matter. This heat of fusion can be measured by a number of thermal techniques, the most popular being DSC. If the heat of fusion of a 100% crystalline material is known, and no significant annealing, or melt/recrystallisation phenomena occur upon heating to the melt, then DSC can quite accurately determine weight fraction crystallinity (see THERMAL CHARACTERIZATION OF POLYMER MATERIALS, E. Turi, Ed., Academic Press, New York, (1980); and Wunderlich, B., MACROMOLECULAR PHYSICS, Academic Press, New York, (1980)).

If the densities of the pure crystalline and pure amorphous material is known then density measurements of a material can yield the degree of crystallinity. This assumes additivity of specific volumes, but this requirement is fulfilled for polymers (or copolymers) of homogeneous

structure. This method depends on careful sample preparation so that no bubbles or large voids exist in the sample.

If purely crystalline and amorphous absorption bands can be identified, then the infrared absorption spectrum offers a convenient way of determining crystallinity (see Tadokoro, H., STRUCTURE OF CRYSTALLINE POLYMERS, John Wiley & Sons, New York, (1979)).

It should be noted that different techniques will often give rise to slightly different values of Φ_C , because they are based on different physical principles. For example, density measurements often give higher values than x-ray diffraction. This is due to the continuous changing of the density in the interface between crystalline and amorphous polymer (or copolymer) material. While x-ray diffraction does not detect this matter as crystalline, density measurements will be affected by this interface region.

For purposes of processing into a film, the PHAs of the present invention preferably have a crystallinity of from about 2% to about 65% as measured via x-ray diffraction; more preferably from about 5% to about 50%; more preferably still from about 20% to about 40%.

Melt Temperature

Preferably, the biodegradable PHAs of the present invention have a melt temperature (T_m) of from about 30°C to about 160°C, more preferably from about 60°C to about 140°C, more preferably still from about 90°C to about 120°C.

Absorbent Articles

The present invention further relates to absorbent articles comprising a PHA of the present invention. Such absorbent articles include, but are not limited to, infant diapers, adult incontinent briefs and pads, and feminine hygiene pads and liners. Films of the present invention used as liquid impervious backsheets in absorbent articles of the present invention, such as disposable diapers, typically have a thickness of from 0.01 mm to about 0.2 mm, preferably from 0.012 mm to about 0.051 mm.

In general, the liquid impervious backsheet is combined with a liquid pervious topsheet and an absorbent core positioned between the topsheet and the backsheet. Optionally, elastic members and tape tab fasteners can be included. While the topsheet, the backsheet, the absorbent core and elastic members may be assembled in a variety of well known configurations, a preferred diaper configuration is described generally in

U.S. Patent 3,860,003, entitled "Contractible Side Portion for Disposable Diaper" which issued to Kenneth B. Buell on January 14, 1975.

The topsheet is preferably, soft-feeling, and non-irritating to the wearer's skin. Further, the topsheet is liquid pervious, permitting liquids to readily penetrate through its thickness. A suitable topsheet may be manufactured from a wide range of materials such as porous foams, reticulated foams, apertured plastic films, natural fibers (e.g., wood or cotton fibers), synthetic fibers (e.g., polyester or polypropylene fibers) or from a combination of natural and synthetic fibers. Preferably, the topsheet is made of a hydrophobic material to isolate the wearer's skin from liquids in the absorbent core.

A particularly preferred topsheet comprises staple-length fibers having a denier of about 1.5. As used herein, the term "staple-length fibers" refers to those fibers having a length of at least about 16 mm.

There are a number of manufacturing techniques which may be used to manufacture the topsheet. For example, the topsheet may be woven, non-woven, spunbonded, carded, or the like. A preferred topsheet is carded, and thermally bonded by means well known to those skilled in the fabrics art. Preferably, the topsheet has a weight from about 18 to about 25 g/m², a minimum dried tensile strength of at least about 400 g/cm in the machine direction, and a wet tensile strength of at least about 55 g/cm in the cross-machine direction.

The topsheet and the backsheet are joined together in any suitable manner. As used herein, the term "joined" encompasses configurations whereby the topsheet is directly joined to the backsheet by affixing the topsheet directly to the backsheet, and configurations whereby the topsheet is indirectly joined to the backsheet by affixing the topsheet to intermediate members which in turn are affixed to the backsheet. In a preferred embodiment, the topsheet and the backsheet are affixed directly to each other in the diaper periphery by attachment means such as an adhesive or any other attachment means known in the art. For example, a uniform, continuous layer of adhesive, a patterned layer of adhesive, or an array of separate lines or spots of adhesive may be used to affix the topsheet to the backsheet.

Tape tab fasteners are typically applied to the back waistband region of the diaper to provide a fastening means for holding the diaper on the wearer. The tape tab fasteners can be any of those well known in the art,

such as the fastening tape disclosed in U.S. Patent 3,848,594 issued to Kenneth B. Buell on November 19, 1974. These tape tab fasteners or other diaper fastening means are typically applied near the corners of the diaper.

Preferred diapers have elastic members disposed adjacent the periphery of the diaper, preferably along each longitudinal edge so that the elastic members tend to draw and hold the diaper against the legs of the wearer. The elastic members are secured to the diaper in an contractible condition so that in a normally unrestrained configuration the elastic members effectively contract or gather the diaper. The elastic members can be secured in an contractible condition in at least two ways. For example, the elastic members may be stretched and secured while the diaper is in an uncontracted condition. Alternatively, the diaper may be contracted, for example, by pleating, an elastic member secured and connected to the diaper while the elastic members are in their relaxed or unstretched condition.

The elastic members may take a multitude of configurations. For example, the width of the elastic members may be varied from about 0.25 mm to about 25 mm or more; the elastic members may comprise a single strand of elastic material or the elastic members may be rectangular or curvilinear. Still further, the elastic members may be affixed to the diaper in any of several ways which are known in the art. For example the elastic members may be ultrasonically bonded, heat and pressure sealed into the diaper using a variety of bonding patterns, or the elastic members may simply be glued to the diaper.

The absorbent core of the diaper is positioned between the topsheet and backsheet. The absorbent core may be manufactured in a wide variety of sizes and shapes (e.g., rectangular, hour-glass, asymmetrical, etc.) and from a wide variety of materials. The total absorbent capacity of the absorbent core should, however, be compatible with the designed liquid loading for the intended use of the absorbent article or diaper. Further, the size and absorbent capacity of the absorbent core may vary to accommodate wearers ranging from infants through adults.

A preferred embodiment of the diaper has an hour-glass shaped absorbent core. The absorbent core is preferably an absorbent member comprising a web or batt of airfelt, wood pulp fibers, and/or a particulate absorbent polymeric composition disposed therein.

Other examples of absorbent articles according to the present invention are sanitary napkins designed to receive and contain vaginal discharges such as menses. Disposable sanitary napkins are designed to be held adjacent to the human body through the agency of a garment, such as an undergarment or a panty or by a specially designed belt. Examples of the kinds of sanitary napkins to which the present invention is readily adapted are shown in U.S. Patent 4,687,478, entitled "Shaped Sanitary Napkin With Flaps" which issued to Kees J. Van Tilburg on August 18, 1987, and in U.S. Patent 4,589,876, entitled "Sanitary Napkin" which issued to Kees J. Van Tilburg on May 20, 1986. It will be apparent that the films of the present invention comprising a PHA of the present invention described herein may be used as the liquid impervious backsheet of such sanitary napkins. On the other hand it will be understood the present invention is not limited to any specific sanitary napkin configuration or structure.

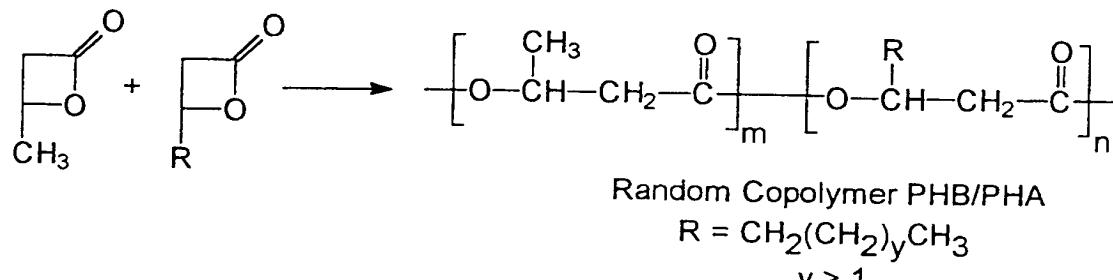
In general, sanitary napkins comprise a liquid impervious backsheet, a liquid pervious topsheet, and an absorbent core placed between the backsheet and the topsheet. The backsheet comprises a PHA of the present invention. The topsheet may comprise any of the topsheet materials discussed with respect to diapers.

Importantly, the absorbent articles according to the present invention are biodegradable and/or compostable to a greater extent than conventional absorbent articles which employ materials such as a polyolefin (e.g., a polyethylene backsheet).

Synthesis of Biodegradable PHAs

The biodegradable PHAs of the present invention can be synthesized by synthetic chemical or biological based methods. A chemical approach involves the ring-opening polymerization of β -lactone monomers as described below. The catalysts or initiators used can be a variety of materials such as aluminoxanes, distannoxanes, or alkoxy-zinc and -aluminum compounds (see Agostini, D.E., J.B. Lando, and J.R. Shelton, POLYM. SCI. PART A-1, Vol. 9, pp. 2775-2787 (1971); Gross, R.A., Y. Zhang, G. Konrad, and R.W. Lenz, MACROMOLECULES, Vol. 21, pp. 2657-2668 (1988); and Dubois, P., I. Barakat, R. Jérôme, and P. Teyssié, MACROMOLECULES, Vol. 26, pp. 4407-4412 (1993); Le Borgne, A. and N. Spassky, POLYMER, Vol. 30, pp. 2312-2319 (1989); Tanahashi, N., and Y. Doi, MACROMOLECULES, Vol. 24, pp. 5732-5733 (1991); Hori, Y., M. Suzuki, Y. Takahashi, A. Ymaguchi, and T. Nishishita, MACROMOLECULES, Vol. 26,

pp. 4388-4390 (1993); and Kemnitzer, J.E., S.P. McCarthy, and R.A. Gross, MACROMOLECULES, Vol. 26, pp. 1221-1229 (1993)). The production of isotactic polymer can be accomplished by polymerization of an enantiomerically pure monomer and a non-racemizing initiator, with either retention or inversion of configuration of the stereocenter, or by polymerization of racemic monomer with an initiator which preferentially polymerizes one enantiomer. For example:



The naturally derived PHAs of the present invention are isotactic and have the R absolute configuration at the stereocenters in the polymer backbone. Alternatively, isotactic polymers may be made where the configuration of the stereocenters is predominantly S. Both isotactic materials will have the same physical properties and most of the same chemical reactivities except when a stereospecific reagent, such as an enzyme, is involved. Atactic polymers, polymers with random incorporation of R and S stereocenters, can be produced from racemic monomers and polymerization initiators or catalysts that show no preference for either enantiomer while such initiators or catalysts often polymerize monomers of high optical purity to isotactic polymer (e.g., distannoxane catalysts) (see Hori, Y., M. Suzuki, Y. Takahashi, A. Yamaguchi, T. Nishishita, MACROMOLECULES, Vol. 26, pp. 5533-5534 (1993)). Alternatively, isotactic polymer can be produced from racemic monomers if the polymerization catalyst has an enhanced reactivity for one enantiomer over the other. Depending on the degree of preference, separate R or S stereo-homopolymers, stereo-block copolymers, or a mixture of stereo-block copolymers and stereo-homopolymers may be produced (see Le Borgne, A. and N. Spassky, N., POLYMER, Vol. 30, pp. 2312-2319 (1989); Tanahashi, N., and Y. Doi, MACROMOLECULES, Vol. 24, pp. 5732-5733 (1991); and Benvenuti, M. and R.W. Lenz, J. POLYM. SCI.: PART A: POLYM. CHEM., Vol. 29, pp. 793-805 (1991)). Some initiators or catalysts are known to produce

predominantly syndiotactic polymer, polymers with alternating R and S stereocenter repeat units, from racemic monomer (see Kemnitzer, J. E., S.P. McCarthy and R.A. Gross, MACROMOLECULES, Vol. 26, pp. 1221-1229 (1993)) while some initiators or catalysts may produce all three types of stereopolymers (see Hocking, P. J. and R.H. Marchessault, POLYM. BULL., Vol. 30, pp. 163-170 (1993)).

For example, preparation of poly(3-hydroxybutyrate-co-3-hexanoate-co-3-hydroxyalkanoate) copolymers wherein the 3-hydroxyalkanoate comonomer is a 3-alkyl- β -propiolactone wherein the alkyl group is at least 3 carbons long, are carried out in the following manner. Proper precautions are made to exclude air and moisture. The lactone monomers (purified, dried, and stored under inert atmosphere), β -butyrolactone and a 3-alkyl- β -propiolactone in the desired molar ratio, are charged via syringe or canula to an oven-dried, argon-purged, and flamed borosilicate-glass tube or flask capped with a rubber septum. The polymerization catalyst is added as a toluene solution via syringe. The tube is carefully swirled to mix the reagents (but not contact the rubber septum) and then heated in an oil bath at the desired temperature for the prescribed time. As the reaction proceeds the mixture becomes viscous and may solidify. If isotactic polymer is produced, solid polymer precipitates out until the entire mass solidifies. The product can then be cooled, removed from the tube, and rid of residual monomer by vacuum drying. Alternatively, the product can be dissolved in an appropriate solvent (e.g., chloroform) and recovered by precipitation in a nonsolvent (e.g., ether-hexane mixture, 3:1 v/v), and vacuum dried. Molecular weight is determined by standard methods such as size exclusion chromatography (SEC, also known as gel permeation chromatography or GPC). The comonomer content of the polymers is determined by nuclear magnetic resonance (NMR).

In a preferred method of synthesizing the PHAs of the present invention, the initiator is an alkylzinc alkoxide, as disclosed in the US Patent Application entitled "Polymerization of Beta-Substituted-Beta-Propiolactones Initiated by Alkylzinc Alkoxides", L.A. Schechtman and J.J. Kemper, assigned to The Procter and Gamble Company, filed January 28, 1994. Such initiators have the general formula R^1ZnOR^2 , wherein R^1 and R^2 are independently a C₁-C₁₀ alkyl. In a preferred method of synthesis, the initiator is selected from the group consisting of ethylzinc isopropoxide,

methylzinc isopropoxide, ethyl zinc ethoxide, or ethylzinc methoxide; more preferably ethylzinc isopropoxide.

Other copolymers useful in the present invention can be made by substituting the starting materials (monomers) in the above procedure with 3-alkyl- β -lactones corresponding to the monomer units desired in the final copolymer product.

Alternatively, biological synthesis of the biodegradable PHAs useful in the present invention may be carried out by fermentation with the proper organism (natural or genetically engineered) with the proper feedstock (single or multicomponent). The production of poly(3-hydroxyalkanoate-co-3-hydroxybutyrate) by *Aeromonas caviae* is disclosed in European Patent Application No. 533 144, Shiotani and Kobayashi, published March 24, 1993. Biological synthesis may also be carried out with botanical species genetically engineered to express the copolymers of interest (see World Patent Application No. 93-02187, Somerville, Poirier and Dennis, published February 4, 1993; and U.S. Patent Application Serial No. 08/108,193, Somerville, Nawrath and Poirier, filed August 17, 1993; and Poole, R., SCIENCE, Vol. 245, pp. 1187-1189 (1989)).

EXAMPLE 1

Poly(3-hydroxybutyrate-co-hydroxyhexanoate)

Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHB-Hx) is prepared according to the general methods described above and based on the published procedure of Hori *et al.* (Hori, Y., M. Suzuki, Y. Takahashi, A. Yomaguchi, and T. Nishishita, MACROMOLECULES, Vol. 26, pp. 5533-5534 (1993)) for the polymerization of β -butyrolactone. Specifically, purified [S]-3-methylpropiolactone ([S]- β -butyrolactone) (9.50 g, 110 mmol) and [S]-3-propylpropiolactone (0.66 g, 5.8 mmol) are charged into a septum sealed, argon purged, dry, glass tube via syringe. The initiator, 1,3-dichloro-1,1,3,3-tetrabutyldistannoxane prepared according to R. Okawara and M. Wada, (J. ORGANOMET. CHEM. (1963), Vol. 1, pp. 81-88) and dried overnight in vacuo at 80°C is dissolved in dry toluene to make a 0.18 M solution. Via syringe, 0.65 mL of the initiator solution (0.12 mmol distannoxane) is added to the tube. The tube is gently swirled to mix the contents and then heated at 100°C for 4 h by immersing its lower half in an oil bath. As the reaction proceeds, the contents of the tube become viscous. After the required time, the tube is removed from the oil bath and allowed to cool to room temperature. The solid is dissolved in chloroform. It is recovered by

precipitation into a hexane-ether mixture, collected by filtration, and dried under vacuum. The comonomer composition of the copolymer is determined by $^1\text{H-NMR}$ spectroscopy and found, within experimental error, to be the same as the charge ratio (95:5). Molecular weight is determined by size exclusion chromatography with chloroform as the mobile phase, and narrow polystyrene standards are used for calibration.

EXAMPLE 2

Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate-co-3-hydroxyoctanoate)

Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate-co-3-hydroxyoctanoate) is prepared by following the same procedure as in Example 1, with the exception that [S]-3-methylpropiolactone (9.50 g, 110 mmol), [S]-3-propylpropiolactone (0.40 g, 3.5 mmol) and [S]-3-pentylpropiolactone (0.50 g, 3.5 mmol) are used as the monomer charge.

EXAMPLE 3

Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate-co-3-hydroxydecanoate)

Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate-co-3-hydroxydecanoate) is prepared by following the same procedure as in Example 1, with the exception that [S]-3-methylpropiolactone (9.50 g, 110 mmol), [S]-3-propylpropiolactone (0.40 g, 3.5 mmol) and [S]-3-heptylpropiolactone (0.60 g, 3.5 mmol) are used as the monomer charge.

EXAMPLE 4

Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate-co-3-hydroxyheptanoate)

Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate-co-3-hydroxyheptanoate) is prepared by following the same procedure as in Example 1, with the exception that [S]-3-methylpropiolactone (9.50 g, 110 mmol), [S]-3-propylpropiolactone (0.40 g, 3.5 mmol) and [S]-3-butylpropiolactone (0.45 g, 3.5 mmol) are used as the monomer charge.

EXAMPLE 5

Compostable Single Layer Film

PHB-Hx of composition 8 mole% hexanoate/ 92 mole% butyrate is introduced into a single screw extruder (Rheomix Model 202) with screw diameter of 0.75 inch. A constant taper screw having 20:1 length to diameter ratio and a 3:1 compression ratio is employed. The temperature of both heating zones of the extruder barrel is 25°C above the melt temperature of the PHB-Hx. The extruder is equipped with a die of width 6 inch and a die gap of 0.04 inch. The die is maintained at 20°C above the

melt temperature of the PHB-Hx. The copolymer is melted within the extruder and pumped to the die at the other end of the extruder. The screw rpm is kept constant at 30 rpm. The copolymer is forced through the die and is collected on a take-up roll collection system (Postex) at a rate that allows crystallization of the copolymer before take-up. The width of these films are nominally 4 inch and the thickness are approximately 0.002 inch.

EXAMPLE 6**Compostable Single Layer Film**

Films of PHB-Hx are made by melting the material between Teflon sheets in a Carver Press (Fred S. Carver Inc., Menomonee Falls, WI) at 20°C above the melt temperature. Pressure on the sheets are adjusted to produce films of approximately 0.25 mm thick. The films are then identically cooled to room temperature by placing the molds between large (5 kg) aluminum plates and allowing the films to cool to room temperature.

EXAMPLE 7**Compostable Multilayer Film**

Sheets of PHB-Hx film may be prepared as in Example 6. These sheets may then encase a sheet of a polymer with good oxygen barrier properties but a poor water vapor transmission rate, or a polymer film that may be water soluble such a poly(vinyl alcohol) (PVA). The films are placed in carver press stacked in the following order PHB-Hx(95:5), PHB-Hx(50:50), PVA, PHB-Hx(50:50), PHB-Hx(95:5). The material is then pressed at a temperature 5°C above the melt temperature of PHB-Hx(50:50), but still below the melting temperature of the PHB-Hx(95:5). After compression at 2000 lb for 30 min, the pressure is released and the film is allowed to cool to room temperature.

EXAMPLE 8**Compostable Disposable Diaper**

A disposable baby diaper according to this invention is prepared as follows. The dimensions listed are for a diaper intended for use with a child in the 6-10 kilogram size range. These dimensions can be modified proportionately for different size children, or for adult incontinence briefs, according to standard practice.

1. Backsheet: 0.020 - 0.038 mm film consisting of a PHB-Hx copolymer (prepared as described in Example 6); width at top and bottom 33 cm; notched inwardly on both sides to a width-at-center of 28.5 cm; length 50.2 cm.
2. Topsheet: carded and thermally bonded staple-length polypropylene fibers (Hercules type 151 polypropylene); width at top and bottom 33 cm; notched inwardly on both sides to a width-at-center of 28.5 cm; length 50.2 cm.
3. Absorbent core: comprises 28.6 g of cellulose wood pulp and 4.9 g of absorbent gelling material particles (commercial polyacrylate from

Nippon Shokubai); 8.4 mm thick, calendered; width at top and bottom 28.6 cm; notched inwardly at both sides to a width-at-center of 10.2 cm; length 44.5 cm.

4. Elastic leg bands: four individual rubber strips (2 per side); width 4.77 mm; length 370 mm; thickness 0.178 mm (all the foregoing dimensions being in the relaxed state).

The diaper is prepared in standard fashion by positioning the core material covered with the topsheet on the backsheet and gluing.

The elastic bands (designated "inner" and "outer", corresponding to the bands closest to, and farthest from, the core, respectively) are stretched to ca. 50.2 cm and positioned between the topsheet/backsheet along each longitudinal side (2 bands per side) of the core. The inner bands along each side are positioned ca. 55 mm from the narrowest width of the core (measured from the inner edge of the elastic band). This provides a spacing element along each side of the diaper comprising the flexible topsheet/backsheet material between the inner elastic and the curved edge of the core. The inner bands are glued down along their length in the stretched state. The outer bands are positioned ca. 13 mm from the inner bands, and are glued down along their length in the stretched state. The topsheet/backsheet assembly is flexible, and the glued-down bands contract to elasticize the sides of the diaper.

EXAMPLE 9

Compostable Lightweight Pantiliner

A lightweight pantiliner suitable for use between menstrual periods comprises a pad (surface area 117 cm²; SSK air felt 3.0 g) containing 1.0 g of absorbent gelling material particles (commercial polyacrylate; Nippon Shokubai); said pad being interposed between a porous formed-film topsheet according to U.S. Patent 4,463,045 and a backsheet which comprises a 0.03 mm thickness PHB-Hx copolymer film, as prepared in accordance with Example 1.

EXAMPLE 10

Compostable Sanitary Napkin

A catamenial product in the form of a sanitary napkin having two flaps extending outward from its absorbent core is prepared using a pad in the manner of Example 9 (surface area 117 cm²; 8.5 g SSK air felt), per the design of U.S. Patent 4,687,478, Van Tillburg, August 18, 1987. The backsheet and topsheet materials are the same as described in Example 6.

EXAMPLE 11

Compostable Disposable Diaper

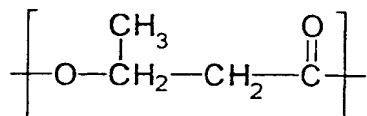
The diaper of Example 9 is modified by replacing the backsheet with a backsheet consisting of a 0.020 to 0.038 mm thickness film comprising a PHB-Hx copolymer film (prepared as described in Example 6).

All publications mentioned hereinabove are hereby incorporated in their entirety by reference.

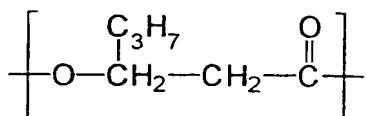
It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to one skilled in the art and are to be included in the spirit and purview of this application and scope of the appended claims.

What is Claimed is:

1. A film comprising a biodegradable copolymer, characterized in that the biodegradable copolymer comprises at least two randomly repeating monomer units wherein the first randomly repeating monomer unit has the structure

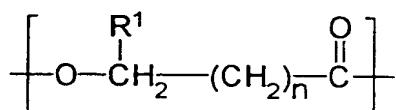


; the second randomly repeating monomer unit has the structure



; and wherein at least 50% of the randomly repeating monomer units have the structure of the first randomly repeating monomer unit.

2. The film of Claim 1, characterized in that the copolymer comprises one or more additional randomly repeating monomer units having the structure

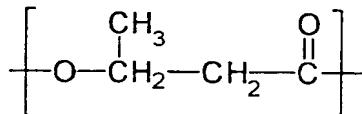


wherein R^1 is H, or a C_2 or $\text{C}_4\text{-C}_{19}$ alkyl or alkenyl; and n is 1 or 2.

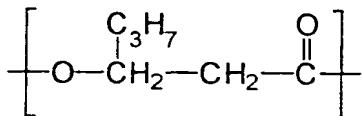
3. The film of Claim 2, characterized in that R^1 is a C_2 or $\text{C}_4\text{-C}_{19}$ alkyl.

4. An absorbent article comprising:

- a liquid pervious topsheet;
- b) a liquid impervious backsheet comprising a biodegradable copolymer, characterized in that the biodegradable copolymer comprises at least two randomly repeating monomer units wherein the first randomly repeating monomer unit has the structure

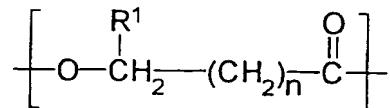


; the second monomer unit has the structure



- ; and wherein at least 50% of the random repeating monomer units have the structure of the first randomly repeating monomer unit; and
- c) an absorbent core positioned between the topsheet and the backsheet.

5. The absorbent article of Claim 4 characterized in that the biodegradable copolymer comprises one or more additional randomly repeating monomer units having the structure



wherein R^1 is H, or a C_2 or C_4-C_{19} alkyl or alkenyl; and n is 1 or 2.

6. The absorbent article of Claim 5, characterized in that R^1 is a C_2 or C_4-C_{19} alkyl.

7. The absorbent article of Claim 4, characterized in that it is in the form of a disposable diaper, sanitary napkin, or pantiliner.

INTERNATIONAL SEARCH REPORT

Internal Application No
PCT/US 95/00585

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08J/18 A61L15/26 A61L15/62 C08G63/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08J A61L C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	<p>MACROMOLECULES, vol.27, no.3, 31 January 1994 pages 878 - 880 EIHAKE SHIMAMURA ET AL. 'PHYSICAL PROPERTIES AND BIODEGRADABILITY OF MICROBIAL POLY(3-HYDROXYBUTYRATE-CO-3-HYDR OXYHEXANOATE)' see page 879, column 2, line 1 - line 21 ---</p>	1
A	<p>WO,A,92 18553 (KOHAP LTD.) 29 October 1992 see page 1, line 10 - line 17; claims 1,2 --- -/-</p>	1-3

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- 'A' document defining the general state of the art which is not considered to be of particular relevance
- 'E' earlier document but published on or after the international filing date
- 'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- 'O' document referring to an oral disclosure, use, exhibition or other means
- 'P' document published prior to the international filing date but later than the priority date claimed

- 'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- 'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- 'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- '&' document member of the same patent family

2

Date of the actual completion of the international search 20 April 1995	Date of mailing of the international search report 04.05.95
--	--

Name and mailing address of the ISA
 European Patent Office, P.B. 5818 Patentiaan 2
 NL - 2280 HV Rijswijk
 Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl.
 Fax (+ 31-70) 340-3016

Authorized officer

Pamies Olle, S

INTERNATIONAL SEARCH REPORT

Intern. Application No.
PCT/US 95/00585

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Week 9306, Derwent Publications Ltd., London, GB; AN 93-049166 (06) & JP,A,5 000 159 (TERUMO CORP.) 8 January 1993 see abstract ---	1-3
A	EP,A,0 226 439 (W.R. GRACE & CO.) 24 June 1987 see claims 1-3,16-18 ---	1-7
A	GB,A,2 243 327 (THE PROCTER & GAMBLE COMPANY) 30 October 1991 see page 4, line 15 - page 5, line 20; claims 1-4,10,11 ---	1-7
A	CHEMICAL ABSTRACTS, vol. 110, no. 19, 8 May 1989, Columbus, Ohio, US; abstract no. 171747t, BRANDL ET AL. 'ABILITY OF THE PHOTOTROPIC BACTERIUM RHODOSPIRILLUM RUBRUM TO PRODUCE VARIOUS POLY(BETA-HYDROXYALKANOATES: POTENTIAL SOURCES FOR BIODEGRADABLE POLYESTERS' page 646 ;column 2 ; see abstract & INT. J. BIOL. MACROMOL., vol.11, no.1, 1989 pages 49 - 55 ---	1-3
A	EP,A,0 533 144 (KANEKA FUCHI KAGAKU KOGYO KABUSHIKI KAISHA) 24 March 1993 see claims 1-5 -----	1-3

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/00585

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A-9218553	29-10-92	AU-A- EP-A-	8612191 0582567	17-11-92 16-02-94
EP-A-0226439	24-06-87	AU-B- AU-A- DE-A- JP-B- JP-A- US-A- US-A-	603076 6601286 3681135 6074340 62209144 4826493 4880592	08-11-90 11-06-87 02-10-91 21-09-94 14-09-87 02-05-89 14-11-89
GB-A-2243327	30-10-91	NONE		
EP-A-0533144	24-03-93	JP-A- US-A-	5093049 5292860	16-04-93 08-03-94